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## LAYER GROWTH OF CdSb PHASE IN THE Cd-Sb DIFFUSION COUPLE AT HIGH PRESSURE

BY MASATAKE KATAYAMA

The layer growth of CdSb formed in the diffusion zone was kinetically investigated by using the Cd-Sb couple over the range of 14–30 kb, 200–280°C and for up to 17 hr. Only CdSb was the reaction product and the region of solid solution was not detectable at either Cd or Sb side. It was found that the layer growth obeyed the parabolic law and Cd atom was by far the faster moving species. From the fact of the parabolic growth and the pronounced Kirkendall effect, the diffusion reaction was adequately explained to occur by the volume diffusion and the vacancy mechanism. Pressure evidently retarded the layer growth; the increase of 8 kb in an applied pressure decreased the rate constant by 10–17%.

The diffusion coefficients of Cd were calculated by using Kidson's method. The activation energies and the volumes obtained for the polycrystal couple were 11–13 kcal/mol in the range of 200–280°C and 1.0–1.7 cm<sup>3</sup>/mol in the range of 14–30 kb, respectively. The diffusion coefficients obtained from the interrelation between Kidson's equation and Heumann's show no significant difference, though the former gives somewhat smaller value than the latter.

### Introduction

The reactivity of metal in solid state is governed by the diffusivity, the vacancy concentration, the dislocation density, and the grain size. Because of the diffusion reaction accompanied with mass flux, these factors raise in a diffusion zone such corresponding results as marker displacement, void formation, climb of edge dislocation and grain boundary diffusion. In 1947, Smigelskas and Kirkendall<sup>1)</sup> first discovered the displacement of the welding interface in the copper-brass couple during annealing. Subsequently, early workers<sup>2,3)</sup> in the field have confirmed that the marker shift which has been usually observed in any couples occurs solely toward the direction of diffusion. Darken<sup>4)</sup> has attributed such the Kirkendall effect to the unequal diffusivities of two atomic species. It has been well established that the diffusion couples showing the Kirkendall effect result from: i) net flux of atoms toward the side of the slower atoms ii) void formation iii) plastic deformation. Owing to the resulting net flux of atoms, the vacancies oppositely flow toward the side of the atom having higher diffusivity. When these vacancies are supersaturated, the voids are produced by the

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\*T/K = 273.2 + (t/°C), 1 bar = 10<sup>5</sup> Pa, 1 μ = 10<sup>-6</sup> m, 1 kcal = 4.184 kJ

1) A.D. Smigelskas and E.O. Kirkendall, *Trans. AIME*, **171**, 130 (1947)

2) L.C.C. da Silva and R.F. Mehl, *ibid.*, **191**, 155 (1951)

3) R.W. Balluffi and L.L. Seigle, *J. Appl. Phys.*, **25**, 607 (1954)

4) L.S. Darken, *Trans. AIME*, **175**, 184 (1948)

precipitation in the diffusion zone<sup>5,6)</sup>. The plastic flow necessarily occurs because the stress arises from the climb of edge dislocations acting as vacancy source and sink<sup>7)</sup>. These general aspects of the Kirkendall effect will give some insights into the mechanism responsible for the diffusion, and so the pure metallic systems having the extended or the restricted solid solubility have been numerous investigated in binary couple from the viewpoint of the Kirkendall effect and the interdiffusion.

It is also said undoubtedly that the study on the diffusion reaction will give further knowledge on the layer growth, and indeed at atmospheric pressure a number of papers have been reported as for the growth kinetics of the intermediate phases exhibiting a definite composition, where in most cases the growth is found to obey the simple parabolic law<sup>8)</sup>. At high pressure more than 1 kb, however, only a few works of this kind have been ever done. The usefulness of an applied pressure can be described as follows: i) stress ensures the contactness of the welding interface and increases the effective cross-sectional area available for interdiffusion; ii) stress tends to diminish or extinguish the Kirkendall voids and relax the restricted flow of atoms. In 1954, Storchheim *et al.*<sup>9)</sup> first studied the effect of pressure on the growth of intermetallic phase formed in Al-Ni system by means of a hot-pressing technique; they reported that increasing pressure decreased the layer width. The similar results were obtained in Al-Ni<sup>10)</sup> and Cu-Zn<sup>11)</sup> systems. Such a pressure-induced decrease in the growth rate seems to be plausible because the interpretation is possible on the basis of the decrease in the diffusivity, whereas a contrary pressure effect has been found in U-Al<sup>12,13)</sup>, U-Ni<sup>14)</sup> and U-Cu<sup>14)</sup> systems. This anomalous pressure-induced increase has not been clearly elucidated. But, at relatively low stress less than 100 bar, it should not be astonishing that the enhanced contactness may produce the stress-induced increase in the growth, and in fact some examples have ever been found<sup>15,16)</sup>.

The diffusion couples made of metal and semi-metal are generally known to form the intermetallic compounds: for example, the intermetallic semiconductors are formed in the II-V group system. In the Cd-Sb system, there exist three phases; CdSb, Cd<sub>3</sub>Sb<sub>2</sub> and Cd<sub>5</sub>Sb<sub>3</sub><sup>17)</sup>. In the Zn-Sb couple the author precedently found a pronounced Kirkendall effect and the pressure-induced decrease in the growth of ZnSb layer<sup>18)</sup>. In this paper, the author deals with the growth of the phase formed in the Cd-Sb couple at quasi-hydrostatic pressure. At quasi-hydrostatic condition different from the case of low pressure, since the stress effects are expected to be conveniently maintained as fixed, the intrinsic

5) F. Seitz, *Acta Met.*, **1**, 355 (1953)

6) R.W. Balluffi, *ibid.*, **2**, 194 (1954)

7) J. Schlipf, *ibid.*, **21**, 435 (1973)

8) Y. Funamizu and K. Watanabe, *Trans. JIM*, **12**, 147 (1971)

9) S. Storchheim, J.L. Zambrow and H.H. Hausner, *J. Metals*, **6**, 269 (1954)

10) L.S. Castleman and L.L. Seigle, *Trans. Met. Soc. AIME*, **212**, 589 (1958)

11) H.A. Froot and L.S. Castleman, *ibid.*, **227**, 838 (1963)

12) A.D. Le Claire and I.J. Bear, *J. Nucl. Energy*, **2**, 229 (1956)

13) L.S. Castleman, *J. Nucl. Mater.*, **3**, 1 (1961)

14) Y. Adda, M. Beyeler, A. Kirianenko and B. Pernot, *Mem. Sci. Rev. Met.*, **57**, 423 (1960)

15) S.K. Behera and L.C. Brown, *Trans. Met. Soc. AIME*, **242**, 2343 (1968)

16) M. Onishi and H. Miura, *Trans. JIM*, **18**, 107 (1977)

17) M. Hansen and K. Anderko, "Constitution of Binary Alloys", p.438, McGraw-Hill, New York (1959)

18) M. Katayama, K. Hara and J. Osugi, *This Journal*, **47**, 42 (1977)

effect of pressure can be extracted.

### Experimentals

Cadmium and antimony metal with the purity of 99.999% were obtained in the form of ingot from Osaka Asahi Metal Co., Ltd. It was guaranteed by emission spectrochemical analysis that the impurities contained in Cd metal were Cu, Si and Mg and those in Sb metal were Cu, Si and As. The diffusion couple was made of both Cd and Sb disks with the shape of 3mm-diameter and roughly 1.5-mm thickness. Tungsten powder was used as the inert marker (about  $3\mu\phi$ ) for the measurement of the Kirkendall effect. In order to exclude the influence of the grain boundary and eliminate any local inhomogeneities, the polycrystal Cd and Sb disks were annealed in vacuum for 30 hr at 200 and 380°C, respectively. The grain sizes obtained were about 0.5mm for both specimens. The Cd (powder)-Sb (polycrystal) couple, denoted as powder Cd couple hereafter, was also used. The disk of Cd powder (99.99%) was made by compression (about 1000 kg/cm<sup>2</sup>) and then sintered for 30 hr at 200°C in vacuum. The pressure apparatus and the construction of the sample cell were previously described in detail<sup>19)</sup>. The diffusion runs were carried out over the range of 200–280°C and 14–30 kb and for up to 17 hr, where temperature was controlled within  $\pm 3^\circ\text{C}$ .

The identification of the reaction product was performed by an X-ray diffraction. The intensities of the characteristic CdL $\alpha$  and SbL $\alpha$  were measured by means of an electron probe microanalyzer (EPMA; Shimadzu EMX), and the scanning profiles were obtained. Concentrations of Cd and Sb in the diffusion zone were determined from the calibration curve which was obtained by calculating the correction factors for atomic number, fluorescence and absorption. The procedure and analysis are the same as already reported<sup>18)</sup>.

### Results

#### Diffusion zone

Fig. 1 (a) shows an X-ray diffraction pattern of the orthorhombic CdSb<sup>20)</sup> synthesized from the

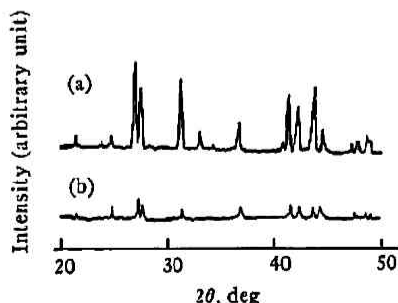


Fig. 1 X-ray diffraction pattern (CuK $\alpha$ ) of (a) CdSb phase synthesized at 400°C and for 3 hr from the 1:1 mixture between Cd and Sb powder, and (b) the product formed in the Cd-Sb couple annealed at 14 kb, 240°C and for 17 hr

19) J. Osugi, K. Shimizu, K. Inoue and K. Yasunami, *This Journal*, **34**, 1(1964)

20) K.E. Almin, *Acta Chem. Scand.*, **2**, 400 (1948)

1:1 mixture between Cd and Sb powder in an evacuated silica tube and Fig. 1 (b) shows that of the product formed in the polycrystal couple. From the good agreement of both patterns the reaction product was identified with the orthorhombic CdSb. Only CdSb was formed above 200°C, and the existence of  $\text{Cd}_3\text{Sb}_2$  and  $\text{Cd}_5\text{Sb}_3$  in the equilibrium phase diagram<sup>17)</sup> was not detected by either EPMA or metallographic observation. The diffusion couple was obviously kept in solid state below 280°C<sup>21)</sup>, whereas at 320°C the phase melted locally at the Cd side because of the Cd-CdSb eutectic (290°C) in the vicinity of the composition of 93 at % Cd<sup>17)</sup>.

Photo. 1 shows a typical microphotograph of the diffusion zone of the polycrystal couple an-

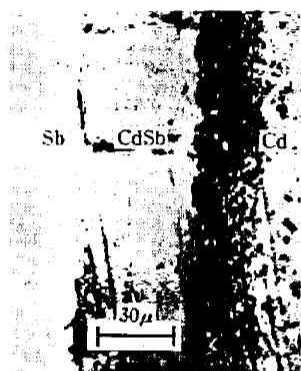


Photo. 1 Typical microphotograph of the diffusion zone in the Cd-Sb couple annealed at 14 kb, 280°C and for 576 min ( $\times 300$ )

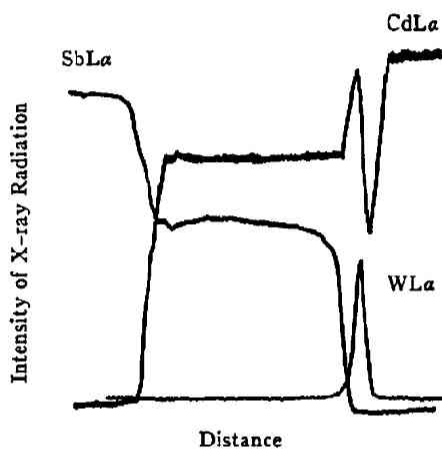


Fig. 2 X-ray intensity-penetration curves for the diffusion zone of photo. 1. Accelerating voltage: 25 kV, Sample current:  $3 \times 10^{-8}$  A, Sample speed: 24  $\mu$ /min

nealed at 14 kb, 280°C and for 576 min. Fig. 2 shows the X-ray intensity-penetration curves obtained from the EPMA line analysis. No appreciable solid solution was formed at either the Cd or the Sb side under the experimental conditions. In both polycrystal and powder couples the tungsten marker moved toward the Cd side with respect to the initial Cd-Sb boundary and the marker was at all times observed at the Cd-CdSb interface as seen in Fig. 2. Such a pronounced Kirkendall effect suggests that the volume diffusion is controlled by the vacancy mechanism and that Cd atoms one-sidedly diffuse faster than Sb at the interface of the marker. Similar phenomenon has been reported in some systems<sup>18, 22)</sup>. Only the diffusion of Cd is focussed on account of the remarkable difference in the diffusivity. As seen in photo. 1, the Kirkendall voids were observed at the Cd-CdSb interface. It was found that the longer annealing time, the more enlarged the number as well as the size of the voids. The couple was easily exfoliated at the Cd-CdSb interface because of the produced voids.

21) G.C. Kennedy and R.C. Newton, "Solids under Pressure", p163, ed. by W. Paul and D.M. Warschauer, McGraw-Hill, New York (1963)

22) H. Miura, Y. Wakamatsu and M. Onishi, *Nippon Kinzoku Gakkaishi (J. Japan Inst. Metals)*, **39**, 903 (1975)

**Layer growth of CdSb phase**

The simple parabolic law is expressed as

$$W = kt^{1/2}, \quad (1)$$

where  $W$  is the layer width,  $t$  the time and  $k$  the rate constant. It has been known that the parabolic law is obeyed when the interface composition remains constant and the movement of the interface is diffusion-controlled. Although the width could be accurately measured within  $1\mu$  with a microscope, the unavoidable uncertainties caused mainly by the non-uniform growth were as much as  $\pm 15\%$ . Fig. 3 shows the layer width of CdSb phase plotted against the square root of the time under various experimental conditions. It is certain that the parabolic rate law is obeyed within the error, and pressure surely retards the growth rate. As seen in Fig. 3, the layer width in a minute was 6–13  $\mu$  in the powder Cd couple. In the case of using the less compressed Cd disk the width was 10–20  $\mu$ . The extraordinary width compared with the polycrystal disk grows probably because the powder disk is not

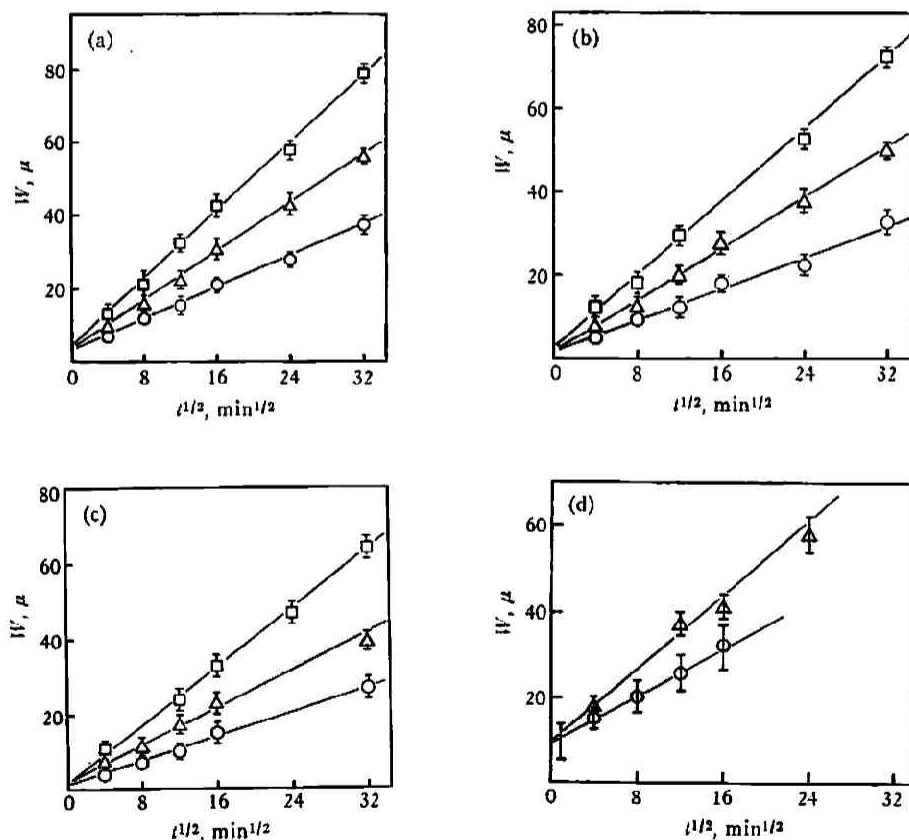


Fig. 3 Layer width of CdSb vs square root of time  
 (a) 14 kb, (b) 22 kb, (c) 30 kb (polycrystal)  
 ○: 200°C, △: 240°C □: 280°C  
 (d) 14 kb (powder)  
 ○: 240°C, △: 280°C

so much dense as the polycrystal one. It seems that the penetration of Sb disk into the Cd side incipiently occurs by shear stress and that the contact interface becomes non-uniform. The initial layer formation may be explained by considering that the interfacial reaction transferring across the interface and the diffusion rapidly take place in the direction normal to the non-uniform interface. After this initial formation, the diffusion was regarded to occur in the growth direction and thus the growth rate was analyzed by deducting  $10\mu$  from the measured layer width. This treatment gives the same activation energy as obtained in the polycrystal couple.

The interface compositions at all the conditions were determined from the EPMA line analysis. Concentrations of Cd,  $C_{\text{CdSb,Cd}}$  and  $C_{\text{CdSb,Sb}}$ , representing the averaged values at the CdSb-Cd interface and those at the CdSb-Sb interface, were 55.2 and 51.7 at% at 14 kb, 53.8 and 50.5 at% at 22 kb, and 53.7 and 50.6 at% at 30 kb. Concentration for the powder couple agreed well with those for the polycrystal. Increasing pressure from 14 to 22 kb tended to lower the Cd concentration slightly, but temperature did not appreciably affect the values. At the fixed temperature and pressure, the compositions exhibited no systematic change with time and their variations with time were within  $\pm 0.5$  at%. The concentration gradient was almost linear in the diffusion zone.

It is conventional to express the concentration as a function of a single parameter  $x/t^{1/2}$ , where  $x$  is the displacement from the Matano interface<sup>23)</sup>. Here, at the fixed pressure and temperature the concentration can be normalized by  $x/t^{1/2}$ , independent of the time. Fig. 4 shows the relationship between

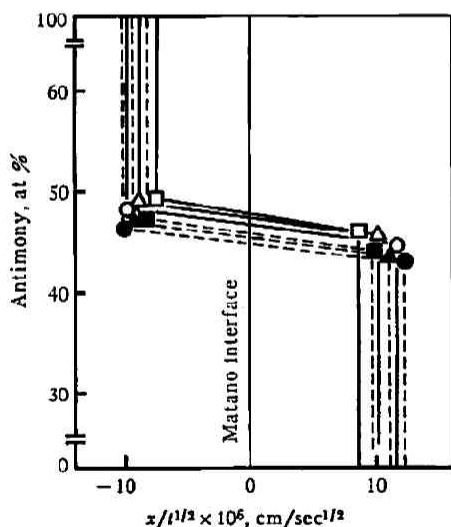


Fig. 4 Antimony concentration vs  $x/t^{1/2}$  for the couples annealed at  $240^\circ\text{C}$   
 ○: 14 kb, △: 22 kb, □: 30 kb (polycrystal)  
 ●: 14 kb, ▲: 22 kb, ■: 30 kb (powder)

Sb concentration and  $x/t^{1/2}$ , where the origin is the Matano interface. When the intermetallic phase with a definite composition is formed, the interdiffusion coefficient,  $D$ , can be calculated by applying either Kidson's equation<sup>24)</sup> or Heumann's<sup>25)</sup>. Both methods can be interrelated as described below.

23) C. Matano, *Japan J. Phys.*, **8**, 109 (1933)

24) G.V. Kidson *J. Nucl. Mat.*, **3**, 21 (1961)

25) T. Heumann, *Z. Phys. Chem.*, **201**, 168 (1952)

By taking into account that the concentration gradient is zero in both Cd and Sb regions, and by assuming that  $D$  and the gradient  $d^2c/dx^2$  are constant in the CdSb layer, Kidson's equation for this three-phase system is modified as

$$D_K = (W^2/t)A, \quad A = \frac{(C_{CdSb,Cd} - C_{Cd,CdSb})(C_{Sb,CdSb} - C_{CdSb,Sb})}{2(C_{CdSb,Sb} - C_{CdSb,Cd})(C_{Sb,CdSb} - C_{CdSb,Sb} + C_{CdSb,Cd} - C_{Cd,CdSb})} \quad (2)$$

where  $C_{Cd,CdSb}$  and  $C_{Sb,CdSb}$  represent Cd at% at the Cd-CdSb interface and that the Sb-CdSb interface. On the other hand, by applying Heumann's equation to this case, Eq. (3) can be derived as shown in the appendix.

$$D_H = (W^2/t)B, \quad B = -\frac{1}{16} + \frac{(C_{CdSb,Sb} + C_{CdSb,Cd})(200 - C_{CdSb,Sb} - C_{CdSb,Cd})}{800(C_{CdSb,Sb} - C_{CdSb,Cd})} \quad (3)$$

It should be noticed that Eqs. (2) and (3) have the same form and both  $A$  and  $B$  are the functions of the concentrations alone. It is also evident that the squared rate constant  $k^2$  equivalent to the term  $W^2/t$  is proportional to  $D$  since  $A$  and  $B$  have a constant value under a fixed pressure. Putting  $C_{Sb,CdSb} = 0$  and  $C_{Cd,CdSb} = 100$ , the difference between  $A$  and  $B$  is consequently

$$B - A = \frac{1}{16} + \frac{(C_{CdSb,Cd} + C_{CdSb,Sb} - 100)^2}{800(100 - C_{CdSb,Sb} + C_{CdSb,Cd})} \quad (4)$$

In the present study the diffusion coefficients of Cd were evaluated by using Eq. (2). The values of  $D$  at 200–280°C were  $7\text{--}34 \times 10^{-10} \text{ cm}^2/\text{sec}$  at 14 kb,  $5\text{--}30 \times 10^{-10} \text{ cm}^2/\text{sec}$  at 22 kb and  $4\text{--}25 \times 10^{-10} \text{ cm}^2/\text{sec}$  at 30 kb. The values of  $k^2$  are summarized with the values of  $A$  in Table 1, where  $k^2$  is the square of the slope in Fig. 3. Figs. 5 and 6 show the temperature and pressure dependence of  $k^2$ , respectively. The activation energies  $E$  and the volumes  $\Delta V^\ddagger$  obtained from Figs. 5 and 6 are listed in Table 2.

Table 1 Squared rate constants  $k^2$  and  $A$  in Eq. (2)

Pressure, kb	Temperature, °C	poly Cd—poly Sb		pow Cd—poly Sb	
		$k^2 \times 10^{10}$ , cm <sup>2</sup> /sec	$A$	$k^2 \times 10^{10}$ , cm <sup>2</sup> /sec	$A$
14	200	2.1	3.4		
	240	4.6	3.3	4.8	3.5
	280	10	3.4	10	3.5
	320	21	3.4	19	3.5
22	200	1.4	3.4		
	240	3.5	3.6	4.2	3.6
	280	8.3	3.6	8.2	3.7
30	200	1.0	3.9		
	240	2.7	3.8	3.3	3.9
	280	6.6	3.7	6.9	3.8
poly: polycrystal		pow: powder			



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Table 2 Activation energies  $E$  and volumes  $\Delta V^\ddagger$  for the Cd-Sb couple in the polycrystal form

Pressure, kb	$E$ , kcal/mol	Temperature, °C	$\Delta V^\ddagger$ , cm <sup>3</sup> /mol
14	11	200	1.7
22	12	240	1.4
30	13	280	1.0

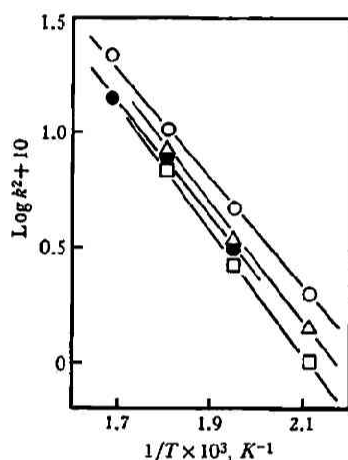


Fig. 5 Plots of  $\log k^2$  against  $1/T$   
 ○: 14 kb, △: 22 kb, □: 30 kb  
 (polycrystal)  
 ●: 14 kb (powder)

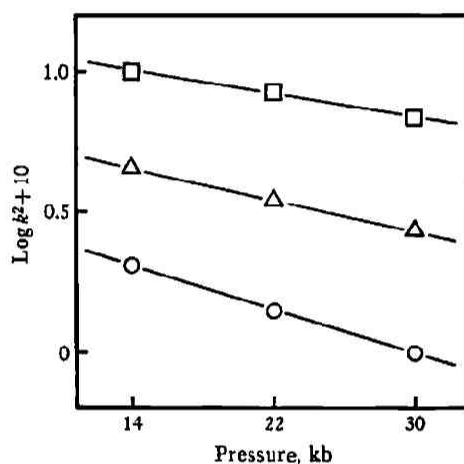


Fig. 6. Plots of  $\log k^2$  against pressure  
 ○: 200°C, △: 240°C, □: 280°C

## Discussion

## Kirkendall effect and growth kinetics

Many binary metallic systems have shown that each component usually diffuses with the comparable rate<sup>8,26)</sup>. In this study the diffusivity of Cd atom is, however, apparently larger by one order of magnitude, or much more, than that of Sb. The result is supported by the other studies on the relative diffusivity. Arakelyan *et al.*<sup>27)</sup> have reported that in the experiment using CdSb single crystal the diffusion coefficient of <sup>125</sup>Sb is much smaller than that of Cd at 300–350°C. In addition, according to Huang *et al.*<sup>28)</sup>, at 180–230°C the coefficient of <sup>124</sup>Sb in tin is small by just one order of magnitude as compared with that of <sup>109</sup>Cd.

26) T. Ustad and H. Sørum, *phys. stat. sol. (a)*, **20**, 285 (1973)

27) Arakelyan, V.S. and Spitsyn, V.I., *Dokl. Akad. Nauk SSSR*, **214**, 1055 (1974)

28) F.H. Huang and H.B. Huntington, *Phys. Rev. B*, **9**, 1479 (1974)

Although both Cd and Sb atoms can move *via* the same vacancies, in this case Cd atoms exchange the site with neighboring vacancies much faster than Sb, and so there occurs a net flux of vacancies equal to the excess flow of Cd atoms toward the Cd side. The Kirkendall voids observed is surely produced by the accumulation of the vacancies. The void formation will be phenomenologically explained by considering that the vacancies locally supersaturate at the Cd-CdSb interface. In the experiment of the effect of pressure on the void formation in Cu-Ni system, Barnes *et al.*<sup>29)</sup> have concluded that the external pressure of about 150 bar reduces the number of voids rather than their size. The finding seems to be a general feature since the voids will disappear by the interdiffusion or the stress-induced plastic flow. But, it is likely that the voids are generated even at higher pressure when there exists a large difference in the diffusivity between Cd and Sb atoms. In the Zn-Sb system the author has also found such a void produced by far the faster Zn diffusion at the Zn-ZnSb interface<sup>18)</sup>.

Since the diffusivity of the vacancies is larger by several orders of magnitude than that of the constituent atoms and a uniform vacancy current is established before the chemical diffusion appreciably takes place, it is, here, fruitful to contemplate the effect of a steady vacancy current in more detail. In the Sb side the vacancies will be generated from the defects such as the dislocations, the grain boundary and the initially existing crack, or from the gas surrounding the couple. On the contrary, the vacancies will be annihilated by the similar defects in the Cd side. Inasmuch as the total number of the lattice sites should remain fixed, in the Sb side the sites are being created and in the Cd side they are being destroyed. If each atomic constituent of the lattice has its own characteristic diffusivity and the density of atoms per unit volume is kept constant, then it is conceivable that the contraction in the Cd side and the expansion in the Sb side could occur in the couple. Smigelskas and Kirkendall<sup>1)</sup> have found that the inner core of the specimen represents the contraction of about 1% when the diffusion zone is about 20% of the core dimension. In this study the ratio of the diffusion zone to the length of the couple is less than 2%. So, it may be estimated that the contraction or the expansion is as much as 0.1%, though the external shear stress under high pressure tends to reduce this plastic deformation.

The effect of pressure on the layer growth has not been clearly understood as yet because the situation differs in the individual system. Here, some factors influencing the growth rate are considerable.

- i) contact cross-sectional area and Kirkendall voids
- ii) volume change
- iii) nucleation and interfacial reaction

Firstly, higher pressure tends to increase the effective cross-sectional area and to repress the formation of the voids. Several examples exhibiting the stress-induced increase in the growth rate have been explained by these factors<sup>15,16)</sup>. High pressure more than 10kb, however, appears to keep the contact area fixed and not to produce so distinct macroscopic change either in number or in size of the voids, though the change in the voids with time may cause the deviation from the parabolic growth.

Secondly, at atmospheric pressure, since the molar volume of CdSb ( $34.3 \text{ cm}^3/\text{mol}$ ) is larger than that of the constituents ( $31.2 \text{ cm}^3/\text{mol}$ ), pressure will give the retarding effect on just the initial nuclea-

29) R.S. Barnes and D.J. Mazey, *Acta Met.*, 6, 1 (1958)

tion at the interface. At high pressure, the molar volume change is unknown. But, in any case, since after the attainment of the initial layer formation the steady diffusion process controls the growth, the volume change itself will not become a factor causing the pressure effect on the growth rate.

Thirdly, it has been believed that the nucleation and the interfacial reaction processes occur so rapidly that the slower diffusion process can not discriminate their effects on overall rate. It has, likewise, not been clear whether pressure influences both processes which may play an important role on the early stage of diffusion. In particular, since any meaningful knowledge on the nucleation process is not obtained by the study of the diffusion reaction, the discussion on its process is made no longer. The interfacial reaction will influence the interface composition. The interface rapidly reaches the local equilibrium, but the slight free-energy difference in the vicinity of the interface motives its shift. From the above reason, the deviation from the equilibrium composition has been often observed at the interface<sup>30,31</sup>. Although the initial departure from the equilibrium composition should be quite large in a couple, in this system the interface composition becomes constant within 15 min. Thus, a steady state is attained in an early stage and then at each pressure the layer parabolically grows as seen in Fig. 3. On the contrary to the present result, if the growth rate is concurrently controlled by the diffusion rate as well as the rate of transfer across the interface, the parabolic law will not be obeyed any longer. Pressure slightly alters the composition. On account of this change the growth rate may be affected in a manner through term  $A$  in Eq. (2). As can be seen in Table 1, the values of  $A$  change a little with pressure, but the pressure-induced decrease in the layer growth will be primarily ascribed to the decrease in the diffusivity of Cd.

#### Diffusion coefficient and activation parameters

As described above, Eq. (2) gives appropriately the diffusivity of Cd in the CdSb zone, though the interdiffusion should be generally considered. Buescher *et al.*<sup>32</sup> reported the self-diffusion of <sup>109</sup>Cd at 251–319°C and 0–8 kb. Their results are listed with the present data in Table 3. At 240–251°C the

Table 3 Diffusion coefficients, activation energies and activation volumes

Pressure, kb	$D \times 10^{10}$ , cm <sup>2</sup> /sec	$E$ , kcal/mol	$\Delta V^*$ , cm <sup>3</sup> /mol	reference
14	16 (240°C)	10.8	1.4	a)
8	4.71 (251°C)	19.8	6.90	b)
a) present data		b) <sup>109</sup> Cd self-diffusion for c-axis direction in cadmium		

coefficient of Cd is comparatively larger than that for the self-diffusion. Here, let us consider the difference in the coefficients obtained from Eqs. (2) and (3). Since in Eq. (4) the second term in the right-hand side gives the values of 0 to 1/8 even though the concentration changes, the value of

30) J.R. Eifert, D.A. Chatfield, G.W. Powell and J.W. Spretnak, *Trans. Met. Soc. AIME*, **242**, 66 (1968)

31) T. Nishizawa and A. Chiba, *Nippon Kinzoku Gakkaishi (J. Japan Inst. Metals)*, **34**, 629 (1970)

32) B.J. Buescher, H.M. Gilder and N. Shea, *Phys. Rev. B*, **7**, 2261 (1973)

$(B-A)$  is in the range of  $1/16$  to  $3/16$ . The value becomes nearly equal to  $1/16$  when both  $C_{\text{CdSb,Sb}}$  and  $C_{\text{CdSb,Cd}}$  are about 50. By making use of the values of  $A$  ( $3.4 < A < 3.9$ ) in Table 1, the ratio of  $B/A$  is estimated to be less than 1.05. This means that Kidson's coefficient  $D_K$  always shows the smaller value in comparison with Heumann's  $D_H$ , though the difference is very small. As a linear concentration gradient is commonly used for the calculation, the difference in the coefficients may arise from the difference in the derivation, that is, the material balance at the interface is considered in Eq. (2) and the Matano-Boltzmann analysis in Eq. (3). The trend that  $D_H > D_K$  agrees with the result which has been found in another system<sup>3)</sup>. Indeed, the resulting ratio of  $B$  calculated from Eq. (3) to  $A$  shows almost the constant value of 1.02 independent of the experimental conditions. Consequently, we need not practically utilize both Eqs. (2) and (3) because the quite similar coefficient is always obtained.

It is unknown whether the chemical diffusion coefficient should be larger or smaller than that for self-diffusion, and how both coefficients depend on temperature and pressure. The difficulty of the direct comparison of the interdiffusion with the self-diffusion consists in the difference of the background that the former is in the presence of the concentration gradient contrary to the latter, and that the defect density is well-defined in the latter but not in the former. In spite of their difference in the situation, the comparison of the activation parameters may be meaningful for the knowledge of the interdiffusion process. As seen in Table 3, the activation energies and volumes are a half and one fifth of those of the self-diffusion, respectively. The author has also obtained the similar trend in the Zn-Sb system<sup>18)</sup>. In considering the pressure effect on the interdiffusion process, the situation becomes much more complicated because the composition around the diffusing species changes a little with pressure. An attempt is made for the interpretation of the large difference in the activation parameters. Since the chemical diffusion occurs by the vacancy mechanism, the parameters will be expressed as the sum of the contribution for vacancy formation and migration as the case of self-diffusion. In quenching experiment of gold, the formation energy  $E_f$  and volume  $\Delta V_f^*$  were 0.95 eV and  $6.8 \text{ cm}^3/\text{mol}$ , and the migration energy  $E_m$  and volume  $\Delta V_m^*$  were 0.94 eV and  $1.5 \text{ cm}^3/\text{mol}$ <sup>33, 34)</sup>, respectively. The trends that  $E_f \geq E_m$  and  $\Delta V_f^* \geq \Delta V_m^*$  are generally found in many self-diffusion processes. And so, the parameters of Cd self-diffusion are also regarded to come from the two parts whose contributions may be in accord with the above trends. From the fact that the interdiffusion coefficient is larger than that of the self-diffusion, more vacancies will be available in the Cd-Sb system. If the vacancy generation can occur more easily or the excess vacancies exist in advance in the initial non-equilibrium state, being almost independent of temperature and pressure, the part of the vacancy formation in the interdiffusion will less contribute to the activation parameters compared with the case of the self-diffusion. Thus, the decrements of both  $E$  and  $\Delta V^*$  qualitatively result.

## Appendix

Assuming a linear concentration gradient within a given phase, Heumann presented Eq. (5),

33) T. Kino and J.S. Koehler, *Phys. Rev.*, **162**, 632 (1967)

34) R.M. Emrick and P.B. McArdle, *ibid.*, **188**, 1156 (1969)

$$D_H = -\frac{W}{2l(C_2 - C_1)} \int_0^{C_{1/2}} x dC, \quad (5)$$

where  $D_H$  is the interdiffusion coefficient,  $W$  the width,  $(C_2 - C_1)$  the concentration difference between both ends of the layer,  $C_{1/2}$  the mean concentration  $[(C_1 + C_2)/2]$ ,  $x$  a distance and  $t$  the time. Fig. 7

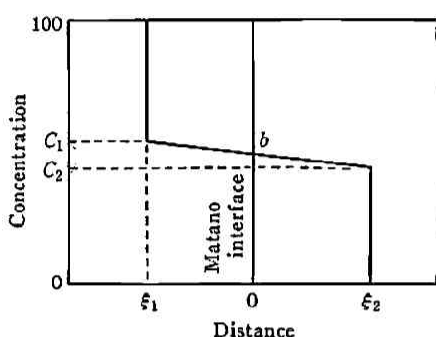


Fig. 7 Schematic representation between the diffusion zone and the interface concentration

shows the typical diagram for a three-phase system, where the interface concentrations ( $C_1$  and  $C_2$ ) are constant and the gradient ( $a$ ) is linear. If we introduce a single parameter  $\xi = x/t^{1/2}$ , the rate constant  $k = W/t^{1/2}$  is replaced by  $(\xi_2 - \xi_1)$  and the boundary conditions are expressed as follows;

$$\begin{aligned} \xi &= \xi_2 & \text{for } 0 \leq C \leq C_2, \\ \xi &= a(C - b) & \text{for } C_2 \leq C \leq C_{1/2}, \end{aligned}$$

where  $C_1 = C_{\text{CdSb, Sb}}$ ,  $C_2 = C_{\text{CdSb, Cd}}$ ,  $a = (\xi_2 - \xi_1)/(C_2 - C_1)$  and  $b = C_{1/2} - (\xi_1 + \xi_2/2a)$ .

Thus, Eq. (5) can be rewritten as

$$D_H = -\frac{W}{2l^{1/2}(C_2 - C_1)} \left\{ \int_0^{C_2} \xi_2 dC + \int_{C_2}^{C_{1/2}} a(C - b) dC \right\}.$$

Integrating Eq. (6) and putting

$$(\xi_2/\xi_2 - \xi_1) = 1 - C_{1/2}/100,$$

which is obtained from Matano's condition, we can derive Eq. (3).

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$$\begin{aligned} \xi_2 - \xi_1 &= 10^6 W_{\text{CdSb}} \sqrt{t} \\ b &= \frac{1}{2} (C_1 + C_2) - \frac{1}{a} (\xi_1 + \xi_2) \end{aligned}$$